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(54) Laminated packaging films and their use

(57) This invention relates to laminated packaging films and containers made from such films, having improved resistance to heat treatment. The said films comprise a heat sealing layer of a copolyamide having a melting point in the range of 120° to 240°C obtained by random copolymerization of precursor monomers of at least two different polyamides. Said laminated films, or the articles formed therefrom such as bags or preformed containers, are useful for packaging applications, particularly in connection with food products.

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SPECIFICATION

Laminated packaging films and their use

This invention relates to laminated packaging films useful, for example, for making bags and pouches, and especially suitable for packaging food products. In the description which follows, the term "packaging materials" refers both to films utilized as such and to bags or other preformed containers manufactured from such films.

Amide homopolymers have been used for several years as components in several types of laminated packaging films, on account of their good mechanical and optical properties, and satisfactory gas barrier capabilities. However, such homopolymers have inferior heat shrinking and welding properties. For these reasons amide homopolymers have been used primarily for non-shrinkable laminated films, in combination with various types of welding layers.

A forward step in the field of amide films has been made with the commercial introduction of a new family of polyamide copolymers obtained using various types and amounts of comonomers.

However, the use of such polyamide copolymers, hereinafter termed copolyamides, in the preparation of films intended for packaging applications, is made problematical, because the gas barrier properties, which, as mentioned, are satisfactory in the case of amide homopolymers, are in this case so weak that the films are no longer impervious to gas. Thus, copolyamides, are used heretofore as backing or "structural" layers to impart strength, required the addition to the laminate of further gas barrier layers and welding layers of various types.

In conventional laminates, whether or not they include a structural layer of copolyamide, polyolefins are generally used for welding or sealing layers which are characterized by low melting points and poor resistance to high temperatures. Thus, and especially in the instance of food products requiring such high temperature heat treatments as sterilization, pasteurization, or cooking, the treatments had to be carried out prior to packaging, with the evident disadvantage that the treated product had to undergo further handling and attendant risk of contaminating it.

Accordingly, while it has been highly desirable to have packaging films available which could withstand high temperature treatment, such that pre-packaged food products can be subjected to thermal treatment, this has been impossible heretofore with conventional films currently in use owing to the poor resistance to heat of the welding layers employed thus far.

The present invention provides a packaging material, particularly intended for food product applications, which has high mechanical characteristics in combination with superior resistance to thermal treatment, even when carried out for extended periods of time and at high temperatures. Packaging film in accordance with the invention has excellent welding properties and is highly resistant to the thermal and mechanical stresses involved in the welding process. It also possesses desirable heat shrinking properties, and good wear resistance.

The heat-shrinkable multiple-layer laminated film of the present invention comprises at least one surface layer including copolyamides obtained by random copolymerization of precursor monomers of at least two different polyamides, said copolyamides having melting points, measured for example on a Perkin Elmer DSC-2 device, in the 120°C to 240°C range. Such films are especially useful for making bags and other containers for packaging food products, at least a portion of the said container being formed by heat welding together two sections of a laminated film according to the invention through their respective heat sealing layers. Such containers are capable of withstanding, without suffering damage to the heat weld, heat treatment at temperatures in the range of 70°C to 120°C for a period of time, which varies inversely with the temperature, from about 10 minutes to about 15 hours.

This invention is based upon the surprising finding that copolyamides may be used in laminated films as surface layers to perform as heat-welding, wear-resistant layers, and as such afford considerable advantages hitherto unattainable with conventional heat-shrinkable laminate films having polyolefinic heat welding layers.

Tests carried out on various types of packages, using each time different thickness dimensions, number, arrangement, or composition of the various layers, have shown that the provision of a copolyamide heat sealing layer in the laminated film affords packages which are resistant to prolonged heat treatment at high temperatures, without prejudice to the integrity of both the welds and film itself, and without the film component layers delaminating or wrinkling.

The copolyamides useful in this invention are obtained by random copolymerization of precursor monomers of at least two different polyamides. As is known, polyamides either derive from the polymerization of a single type of monomer comprising both the chemical functions which are typical of polyamides, i.e. amino and acid groups, such monomers being typically lactams, or from the polycondensation of two types of polyfunctional monomer, i.e. polyamines and polybasic acids.

In the preparation of the copolyamides for use in this invention, therefore, two different lactams may be employed, or two types of polyamines and polyacids, or a lactam on one side and a polyamine and a polyacid on the other.

Thus, the copolyamides which are suitable for use with this invention may be prepared from monomers selected from caprolactam, lauryllactam, w-aminoundecanoic acid, adipic acid, azelaic acid, sebacic acid, undecanedioic acid, terephthalic acid, dodecanedioic acid, hexamethylene diamine, or p-

xylylenediamine. Such copolyamides as are currently available commercially may be used, e.g., those known under the following trademarks: GRILON CA 6 (a Nylon 6/12 containing about 38% of 12 and having a melting range of 135—145°C) and GRILON CR 9 (a Nylon 6/12 containing about 14% of 12 and having a melting range of 197—200°C) (both from EMS Chemie), ULTRAMID C 35 (a nylon 6/6—6 containing about 19% of 6—6 and having a melting range of187—200°C) (from BASF), DURETHAN C 38 F (from Bayer), and NOVAMID 2030 and NOVAMID 2020A (from Mitsubishi). Such copolyamides desirably have melting points in the 120°C to 240°C range.

Expediently, the copolyamides acting as the heat sealing layer are employed in the new laminated films in association with additional layers of various character and in varying number, depending on the specific requirements which the final film is to meet in relation with its intended application.

In particular for use in films intended for packaging food products such as meat, hams, etc., the heat sealing copolyamidic layer may be associated with a backing or structural (or filler) layer capable of imparting the strength required for the application, as well as with a layer having good gas barrier properties.

The gas barrier layer may comprise any polymer conventionally utilized for that purpose, such as a copolymer of ethylene/vinyl alcohol (EVOH), polyvinylidene-chloride (PVDC), or a copolymer thereof.

For the structural or backing layer, any material possessed of good strength properties may be used, e.g. an olefinic polymer or copolymer.

An example of simple structure for a laminated film processed in accordance with this invention is the following:

copolyamide/EVOH/copolyamide.

For very high temperature applications, the adherence of the gas barrier layer to the polyolefinic layers must be inadequate, in which case adhesives can be interposed between the various layers constituting the laminated film.

Examples of laminated films according to the invention which have more than three layers are the following:

INSIDE OUTSIDE

(1) Copolyamide/Adhesive/Filler/PVDC/Protective layer, or

(2) Copolyamide/1st adhesive/2nd adhesive/PVDC/3rd adhesive/Protective layer

wherein the "inside" layer is that devised to contact the food product during packaging application and to be heat sealed.

In these exemplary films, the filler and protective layers may comprise low-cost olefinic materials having good bonding properties for PVDC, e.g. a copolymer of ethylene/vinylacetate (EVA) having a vinyl acetate content of 3 to 30% and a melt flow index of 0.2 to 20. The filler layer may also comprise a polymer not necessarily having good adhesion to PVDC, eg., ethylene or propylene homo- or copolymers.

The adhesive layers may comprise modified olefinic copolymers, such as modified EVA like those available commercially under the trademarks PLEXAR (from CHEMPLEX), ADMER (from MITSUI), OREVAC (from ATO CHEMIE), CXA and SURLYN (from DU PONT), LUPOLEN (from BASF), NOVATEC (from MITSUBISHI), ethylene/ethyl acrylate copolymers (from BP), or copolymers of ethylene/methylacrylate or ethylene/acrylic acid.

The film (2) exemplified above may be suitable for very high temperature applications, where the adherence between PVDC and the filler layers on one side, and the protective one on the other side, may be inadequate and may require the use of several adhesives.

The laminated films of this invention which comprise copolyamide heat sealing layers are especially heat resistant. In particular, the same resistance to heat is also exhibited by the weld made from the heat sealing layers of the invention, where the film is formed into a bag, pouch or other container, or utilized as such and subsequently wrapped around a product and welded thereon.

Thus, unlike conventional films which can withstand a heat shrinking treatment up to a maximum of about 96°C for no more than 1—2 seconds, bags formed from the new laminated film can withstand a pasteurization treatment at 95°C for periods of about 1 hour, a sterilization treatment at about 120°C for periods up to 10 minutes, and a cooking treatment in the prepackaged form at 70°C for periods up to 14 hours.

If a copolyamide layer of appropriate thickness, in the range from 3 to 50 μ is used, laminate films are obtained which are not only highly resistant to heat treatment but also have extremely good properties of wear and abrasion resistance.

In fact, it has been found that the copolyamide layer utilized in this invention has, in addition to excellent characteristics as the inside heat-sealing layer, also good wear, abrasion and puncture resistance properties.

Alternatively, for the high wear-resistant layers, additional copolyamidic layers may b used, in particular as outer layers. In that case, the copolyamide heat sealing layer would have a thickness dimension reduced by 3 μ, resistance to wear being afforded by at least one further copolyamidic outer

layer having a thickness of 10 to 100 μ. Of course, there can be also provided m re copolyamide layers in addition to the two mentioned above, because, as explained, the laminated film of this invention may be made in an unlimited number of variations and with a number of layers which is only limited by considerations of convenience in manufacturing and use. By orienting the laminated films of this invention, or the individual layers composing it, and then laminating said layers, films are obtained which exhibit excellent heat shrinking properties.

The new laminated films may be produced by conventional techniques, by extruding the layers which compose the film, and then causing them to adhere together, and/or by tubular co-extrusion thereof, and subsequent stretching and orientation, e.g. in a blown up bubble, so as to obtain a heat shrinkable film.

Articles of manufacture, for example bags and other containers can be formed from the laminated films using any suitable technique. For example a tubular co-extruded film may be flattened, transversely heat sealed and severed to produce end-seal bags. Bags can also be prepared, which are side-seal bags, by starting from the tubular flattened film, slitting it along one side, making pairs of transverse heat seals and then severing into bags by separating between the pair of transverse seals.

The heat shrinkability of the films of the invention has been shown to be quite satisfactory, as outlined above, and capable of meeting the requirements of the packaging application for which the film is intended.

The transparency of the copolyamide layer, due to the less crystalline nature of such compounds, makes the film ideally suitable for packaging products which are to remain in full view.

The examples which follow illustrate some of the more important aspects of the invention.

EXAMPLE 1

Bags were prepared by heat welding films according to the invention and then tested. The structure of the bags and results of the tests are shown in Table 1 below.

TABLE 1

	1	2	3
Structure	Ny CA 6	Ny CA6/SU /EVA 18%	Ny CA6/SU/Ny CA6
Thickness	35 μ	34 μ 19 μ 29 μ	32 μ 11 μ 25 μ
Shrinkage at 80°C %	T 39 L 36	T 40 L 46	T 39 L 39
at 85°C %	40 38	44 48	46 46
at 95°C %	55 50	49 54	50 54
VPHB at 80°C IOWP*(cm)	60(152)	80(203)	90(229)
at 85°C IOWP(cm)	55(140)	70(178)	84(213)
at 95°C IOWP(cm)	Film breaks	60(152)	55(140)
VPHB with fat			
at 80°C IOWP(cm)	54(137)	80(203)	90(229)
at 85°C IOWP(cm)	52(132)	70(178)	80(203)
at 95°C IOWP(cm)	Film breaks	55(140)	50(127)
Resistance to heat:			
at 70°C × 14 h		good	good
at 95°C × 1 h		good	good
at 120°C × 10 min.		good	good
Bag dimensions (mm)	180 × 360	180 × 360	180 × 360

*IOWP: inch H_2O

where:

Ny CA6 is a copolyamide produced by EMS-CHEMIE;

SU is Surlyn, a registered trademark of DuPont for ionomeric resins of their production;

EVA is a copolymer of ethylene/vinylacetate having an 18% content by weight of vinylacetate;

VPHB is a method developed by the Applicants for evaluating the hot strength of the weld (variable pressure hot burst). The variable pressure hot burst (VPHB) method comprises immersing in hot water a sample (bag) on which a heat seal has been formed, injecting air under increasing pressure (measured in inches or cm of water pressure) and measuring the pressure at which the heat seal breaks.

The values shown give the pressure, expressed as inch (or cm) H_2O, whereat the weld fails. By comparison, commercially currently available heat shrinkable bags reach values in the 10 to 20 inch (25 to 50 cm) range.

Column 1 of the Table shows the properties of a single-layer copolyamide film suitable for use in the laminated films of this invention.

It may be seen from Table 1 that bags formed from films in accordance with this invention (Columns 2 and 3) have excellent heat resisting properties. Moreover, they show good heat shrinking and gas barrier properties.

EXAMPLE 2

Wear and abrasion resistance tests carried out on experimental heat shrinkable bags, such as one made of a laminate having an overall thickness of 130 microns, having ceramic tureens packaged therein, have shown a reject percent, as evaluated after transportation on a truck over distances equal to or exceeding 1,000 km, equal to about 50% less than the rejects resulting from the use of bags having the same thickness and currently used.

A suitable laminate may made, using the technique generally described in USP 4273549, by coating on to a known heat-shrinkable laminate as described in British Specification No. 1392334, sold by the Applicants under the trade name BB-1, and having layers of irradiated ethylene/vinyl acetate copolymer, polyvinylidene chloride, and ethylene/vinyl acetate copolymer, further layers of Surlyn 1652 (as adhesive) and Grilon CA6.

CLAIMS

1. A heat shrinkable multi-layer laminated film comprising at least one surface layer including a copolyamide obtained by random copolymerization of precursor monomers of at least two different polyamides, said copolyamide having a melting point in the range of 120°C to 240°C.

2. Laminated film according to claim 1 wherein the said surface copolyamide layer is a heat sealing layer.

3. Laminated film according to claim 1 or 2, wherein the said polyamide precursor monomers are selected from caprolactam, laurillactam, ω-aminoundecanoic acid, adipic acid, azelaic acid, sebacic acid, undecanedioic acid, terephthalic acid, dodecanedioic acid, hexamethylenediamine and p-xylylenediamine.

4. Laminated film according to claim 1, 2 or 3, comprising, as an additional layer, at least one gas barrier layer.

5. Laminated film according to claim 4, wherein the said gas barrier layer is formed from a copolymer of ethylene/vinyl alcohol (EVOH) or from polyvinylidenechloride.

6. Laminated film according to any of claims1to 5, wherein the said copolyamide layer has a thickness in the range of 3 to 50 μ.

7. Laminated film according to any of claims 1 to 6, comprising a further surface layer of a said copolyamide having a thickness in the range of 10 to 100 μ.

8. Laminated film according to claim 7, wherein the said further copolyamide layer is bioriented and heat-shrinkable.

9. Laminated film according to any of claims 1 to 8 further comprising at least one olefinic protective layer.

10. Laminated film according to any of the preceding claims, wherein the said multiple layers have been at least in part united together by co-extrusion.

11. Laminated film according to any of claims 1 to 9, wherein the said multiple layers have been at least in part united together by the interposition of adhesive layers therebetween.

12. Laminated film according to claim 1 substantially as hereinbefore described.

13. A bag or other container suitable for packaging food to be subjected to heat treatment at a temperature in the range of 70°C to 120°C for a period of time from about 10 minutes to about 15 hours, the said container comprising a laminated film as claimed in any of claims 1 to 12.

14. A bag or other container as claimed in claim 13 adapted to be closed by heat-welding the said laminated film or by clipping.

15. Packaged food product comprising a container formed from a film according to any one of th claims 1 to 12 and a food product which has been heat-treated within said container at 70—120°C for a period from 15 hours to 10 minutes.

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